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QUARTERLY STATUS REPORT #3

SILICON SURFACE PASSIVATION FOR DEVICES

NASA RESEARCH GRANT

NGR 36-003-067

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National Aeronautics & Space Administration
Electronics Research Center
Cambridge, Mass.

F. J. Cocca, Grant Monitor

June 1, 1969

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Professor A. B. Kuper

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CONTENTS

Introduction

In response to the interest of the NASA/ERC sponsoring group in device pre-screen testing expressed to us in our visit to Cambridge April 22, program emphasis this quarter has been shifted more to device pre-screen testing.

Results this quarter have included water-film conductance feasibility studies. This has led to demonstration of a novel pre-screening technique we call (TDQ) Transient Differential Quench. TDQ conductance effect is observed with relatively high humidity.

Approximately 100 encapsulated diodes have been tested, measuring reverse current (I_r) vs. voltage (V), temperature (T) and time (t) using three pre-screen techniques:

(1) I_r vs. V hysteresis, T from T_{room} to 77°K.

(2) I_r vs. t in TDQ, quenching to 0°C.

(3) I_r vs. t after application of V.

Results indicate that (1) may be a useful pre-screen, (3) appears to be a simple pre-screen. Results with (2) on diodes are negative.

I. Research Completed

1. Electrolysis cell was completed for mounting on the quadrapole gas analyzer, with provision for demounting oxidized silicon samples. Fig. 1 shows the essential elements: insulated feeds, sample mount, flange mount to instrument.

2. Interface-States results have been obtained in four main areas:

   a.) analysis of transient MOS C(V) at 77°K.

   b.) relaxation processes at the interface at low T.

c.) annihilation of interface states by hydration.

d.) impurity--interface-state interaction.

The work is being written up and copies of the thesis report will be forwarded to the grant monitor.

3. Water-film Conductance. Preliminary electrical measurements were made in preparation for conductance measurements over the surface of oxide in passivated Si devices. Test set-up is shown schematically in Fig. 2. Here conductance over the surface of the glass header feed-throughs is measured.

Humidity was controlled in the can by use of saturated salt solutions, listed in Table I.

Results are shown in Fig. 3, demonstrating expected results with our set-up. This approach will be used in further work with the electrolysis cell (Fig. 1) as time permits.

As originally proposed, the possibility of an easily-identifiable conductance anomaly at the ice-point was investigated. As shown in Fig. 4 the effect is seen at high humidity over test glass. It may be possible to use this effect to distinguish surface-related failure in pre-screening of devices.

4. TDQ (Transient Differential Quench). An idea developed out of the lowered-temperature testing with the test jig. of Fig. 1. We reasoned that a transient test might distinguish surface conductance over oxide from bulk conductance. If the can or other surface were cooled faster than the sample, ions and water film might be distilled from the sample.

This idea which we call TDQ (Transient Differential Quench), was tested by quenching from room temperature to slightly below 0°C. In

Table I

CONTROL OF R.H. BY SATURATED AQUEOUS SALT SOLUTIONS

% R.H. at 25°C	Salt	gms/100 ml. H_2O for saturation
0%	Drierite	
12	L_iCl	64g.
33	$MgCl_2 \cdot 6H_2O$	167
66	$NaNO_3$	100
80	NH_4SO_4	76
100	distilled H_2O	

Fig. 1 a copper tube is shown connected to the test header. In this case, sample glass feed-throughs on the header cooled approximately at the same rate as did the outer copper can. By removing the copper tube, the header was isolated, and cooled more slowly than the can after quench, finally equilibrating.

Results in Fig. 5 show that the TDQ effect on conductance of test glass at high humidity is easily seen. A remarkable delay of almost 6 minutes occurred.

By measuring an appropriately sensitive parameter, this simple technique might detect incipient surface failure in devices.

II. Research in Progress

1. Time-Dependent Device Pre-screening

A. TDQ on Commercial Diodes

Having demonstrated that a TDQ effect could be seen on glass surface conductance in humid encapsulation, we investigated TDQ as a pre-screen technique on commercial off-the-shelf transistor pn junctions, using reverse current as test parameter.

This test offers the possibility of pre-screening bad encapsulations or surface-dependent devices which have passed static testing. The method consists of quenching sample and can at different rates and measuring parameter of interest as a function of time. It is intended to be a new way to identify surface versus bulk conduction. It should require a conveniently small temperature excursion. It may have advantages over static tests, and require no absolute calibration. It must be emphasized that in these device tests: (1) we do not expect many "bad" units which show TDQ effect and (2) reverse current may not be a sufficiently sensitive parameter at such low humidity.

Test jig for TDQ TO-5 headers is shown in Fig. 6. Header copper fin is immersed in the cold reference bath at start of timing quench. Upper copper fin connected to can may be heated to accentuate desorption from can. The jig may also be inverted. Current is measured with a Keithley 610.

Three transistor types used in these tests are listed in Table II. Moderately high breakdown collector junctions were used. P-type collectors are expected to be more sensitive because of the known tendency for oxidized Si surfaces to tend n-type. Thus two of the transistors selected are pnp. Likewise a range of junction areas was selected, as seen by C_{OB}, to accentuate junction perimeter effects. Power device would be expected to have best heat-sinking.

Before transient testing, static I_{CBO}-V_{CB} data were taken on all transistors, shown in Figs. 7-10. These will be referred to later. Note the wide range of characteristics on these off-the-shelf devices. One of each code is actually outside of specification (Table II).

TDQ showed no effect, as shown in Fig. 11 for collector diodes quenched to an ice-bath from room temperature and also using the heated fin. The system seemed well-behaved, with header-quenching resulting in faster cooling than when the fins were reversed and can was quenched. Note that current relaxed in about one minute and the effect was similar at microampere and nanoampere ranges.

Thus we have not found a TDQ effect in devices. The work we have done suggests the following, however:

(1) TDQ might be seen using a more sensitive parameter. We consider pre-avalanche noise as a possibility.

Table II

SILICON TEST TRANSISTOR PARAMETERS

	2N3053	2N2904	2N3741
Mfgr.	RCA	MOT.	MOT.
Config.	NPN	PNP	PNP
Type	Planar	Epi, Annular	-----
Power	medium	low	high
f_T (MHz)	20	200	-----
Header	TO-5	TO-5	power
V_{CBO} (max.V)	60	60	80
I_{CBO} (max)	0.25 ua (30v)	0.02 ua (50v)	0.1 ma (60v)
C_{OB} (pf. max, 10v)	15.	8.	100.
Thermal res. jcn-base	35°C/w.	----	----

(2) The test is simple and non-perturbing.

(3) We have introduced the possibility of <u>time</u> as a pre-screening parameter.

B. I_{CBO} vs Time as a Pre-screen

TDQ experiments revealed a detectable time-dependence of I_{CBO} at constant V_{CB} which we next investigated. We noted that quench results depended on timing of the application of voltage to the diode as well as on timing of start of quench.

The most significant result is shown in Fig. 12 where relaxation of diode no. 6 continues for almost one minute after reverse bias is applied at room temperature. The standard state for these tests was diode short-circuited before t = 0. The important point to note is that static I_{CBO} vs V_{CB} in Fig. 7 shows virtually no difference between diodes #6 and #7. The result of Fig. 12 suggests that diode 7 shows overshoot and relaxation characteristic of the long time-constants of the system. With the same system settings, #6 shows, in addition, a clearly observable longer time constant. This suggests device surface time-dependence in diode #6. Thus we have a simple transient test which may be useful as a pre-screen.

Current in Fig. 12 saturates at about 25 nA as indicated. (Note in Figs. 12-17 that zero of current has been suppressed in the plots.)

In Fig. 13 the transient test is applied to a family of large n^+p diodes of the same code and nearly the same current at 10v (see Fig. 7). Here the "soft" diode shows a large, very noisy, slow relaxation, indicating surface and possible hermeticity problems.

Note however that a "soft" diode need not be surface-dependent, as shown in Fig. 14. Using a family of small n^+p diodes, we see that the soft diode has much higher current at 30v (see also Fig. 8) but shows only system relaxation. We conclude that diode #4 in this case is bulk-, not outer-surface-shunted.

It was found that the high impedance of the Keithley 610 could lead to change in relaxation if range were changed. This is shown in Fig. 15 where overshoot characteristic of I_{CBO} vs time changes as current ranges change. Thus a valid pre-screen test should compare devices against reference devices at the same system settings.

Fig. 16 shows that very little change is seen in a "good" device by performing the transient test at 0°C as compared to room temperature. Also shown is comparison of diode response to that of a resistor. It can be seen that, in the 1uA range, diode introduces relaxation for about 2 sec, which is short compared to the long times we attribute to surface instability.

In Fig. 17 we show effect of V_{CB} on relaxation of a "good" diode. Choice of constant V_{CB} does not appear to be critical.

Thus we have found a simple pre-screen test which:

(1) reveals anomalies in a population, not seen in static test.

(2) may distinguish between surface and bulk incipient failure.

(3) Is easily interpreted, if system RC is held constant.

2. Low Temperature Device Pre-screening

Following the initial work of F. Cocca at ERC, low temperature hysteresis measurements of the reverse bias voltage current characteristic as a possible pre-screening test have been initiated this quarter. Cocca's results indicate that the direction of hysteresis could possibly be used to differentiate between bulk defects (i.e. traps etc.) and surface ion conduction.

A test cell was constructed, shown in Figure 18, to investigate these effects. Temperature is controlled by varying the power to the jacket heater, working against a cold reservoir of liquid nitrogen. The test circuit has the capability of plotting a point-by-point voltage characteristic as well as automatically sweeping the diode voltage at a rate of 0.001 Hz to above 10Hz. In order to remove effects of current conduction through moisture condensation across the outside of the diode package, a steady flow of dry nitrogen was maintained across the test diode throughout the temperature cycle.

The instrumentation setup was evaluated for "built in" hysteresis effects by obtaining the V-I characteristics of a 22 meg-ohm carbon resistor. The upper sweep frequency that could be reliably used without introducing readout errors was determined by obtaining the system response to a step input. Fig. 19 indicates the step response of the system. To improve overall response, the system is somewhat undercompensated. The maximum sweep speed will be kept below 0.5Hz to minimize lag in recorder response which can be mistakenly identified as hysteresis.

The devices used in this test were glass-encapsulated 1N3605 diodes. 100 units were used in the evaluation lot. Of the 100 diodes, 5 diodes failed to meet room temperature reverse current leakage tests. The units were separated into two groups. Group A were diodes meeting room temperature specifications and Group B were diodes not meeting specifications. Diodes were then cooled from room temperature to -196°C. V-I characteristics were measured at 25°C increments. The results of these tests are as follows:

(1) Over 20% of the units tested indicated the negative-

going hysteresis characteristics of what Cocca has referred to as a non-ideal diode. Fig. 20b is an example of this hysteresis.

(2) Diodes of Group B did not indicate the hysteresis of non-ideal diodes.

(3) No change in breakdown voltage was seen for diodes exhibiting non-ideal hysteresis.

(4) In some cases hysteresis characteristics changed as the temperature was lowered. Specifically shown in Fig. 20a and b, the hysteresis characteristics of an "ideal" diode were seen at -50°C (Fig. 20a). These characteristics changed at a temperature of -100°C to the non-ideal case.

(5) In some cases, it was possible to produce a negative-going hysteresis by increasing the sweep rate from .01Hz to .05Hz. Increasing the sweep further leads to gross distortion of the V-I characteristic.

In analyzing the results, the most significant result appears to be the fact that diodes which had non-ideal characteristics at low temperatures passed room temperature screening tests. No conclusive results of device hysteresis can be related to device reliability until diode aging tests are carried out.

Future Work

In the next quarter, it is proposed that the tested devices be aged under load conditions to determine the relationship between hysteresis and device reliability.

To more quantitatively evaluate this effect, planar diodes will be constructed with varying passivating oxide thicknesses. These diodes will be hermetically sealed in containers having various levels of relative humidity ranging from less than 1% to greater than 50%. The same hysteresis tests will be performed. The results of this test should indicate the degree of sensitivity of surface ion detection that can be obtained using leakage current phenomena. A complete analysis of this system will then be performed. The possibility of using 1/f noise as a sensitive indicator of surface ion movement will also be investigated.

III. Conclusions and Program Plan

A. Summary of Results and Conclusions

1. Glass surface conductance at high humidities was measured. Humidity dependence and ice-point anomaly were observed.
2. A novel pre-screen technique , Transient Differential Quench (TDQ), was attempted as a new way to identify surface versus bulk conduction. TDQ effect was demonstrated in the case of glass surface conduction at high humidity. The effect has not been seen on encapsulated devices using reverse current as parameter.
3. Our work suggests time relaxation, perhaps in conjunction with lowered-temperature, as a pre-screen technique.
4. Long time-constant reverse-current relaxation has been demonstrated on off-the-shelf devices and is suggested as a simple surface-failure pre-screen.
5. Low temperature hysteresis, follow-up of the work of F. Cocca at ERC, has been measured on glass-encapsulated diodes. It appears to be a possible useful pre-screen.

B. Program Plan

For remainder of grant we plan to:

1. Investigate low temperature hysteresis pre-screen further.
2. Investigate relaxation pre-screen dependence on temperature, especially through 0°C.

3. Inter-compare the two techniques.

4. Stress our diodes to try and correlate with pre-screen results.

5. Measure possible more-sensitive pre-screen parameters.

IV. Personnel, Publications, Equipment

A. Personnel

During this quarter personnel associated with the grant, in addition to Prof. Kuper, have been:

Faculty :	Profs. W. H. Ko and E. T. Yon
Graduate Students:	H. P. Caban-Zeda
Technician :	T. O'Mara

Prof. Kuper and Yon visited NASA/ERC April 22 for discussion. Prof. Yon will be in charge during Prof. Kuper's absence in July and August.

Mr. Caban-Zeda is completing his PhD thesis on Si/SiO_2 interface states low temperature transient effects.

Mr. O'Mara is assisting in the pre-screening experimental program.

B. Publication

"Water Contamination in Thermal Oxide on Silicon", G. L. Holmberg and A. B. Kuper, was presented to the Electrochemical Society, May 6, 1969, New York City. The paper is being submitted to the Journal of that society.

"Combined MOS and Radiochemical Analysis of Impurities in SiO_2 on Si", a review of grant work by Alan B. Kuper, was published this quarter in "Surface Science" 13, 172-183, 1969.

C. Equipment

Keithley 600C, specified in grant budget was purchased this quarter.

Low temperature controllable facility (Fig. 18) was set up this quarter for device testing.

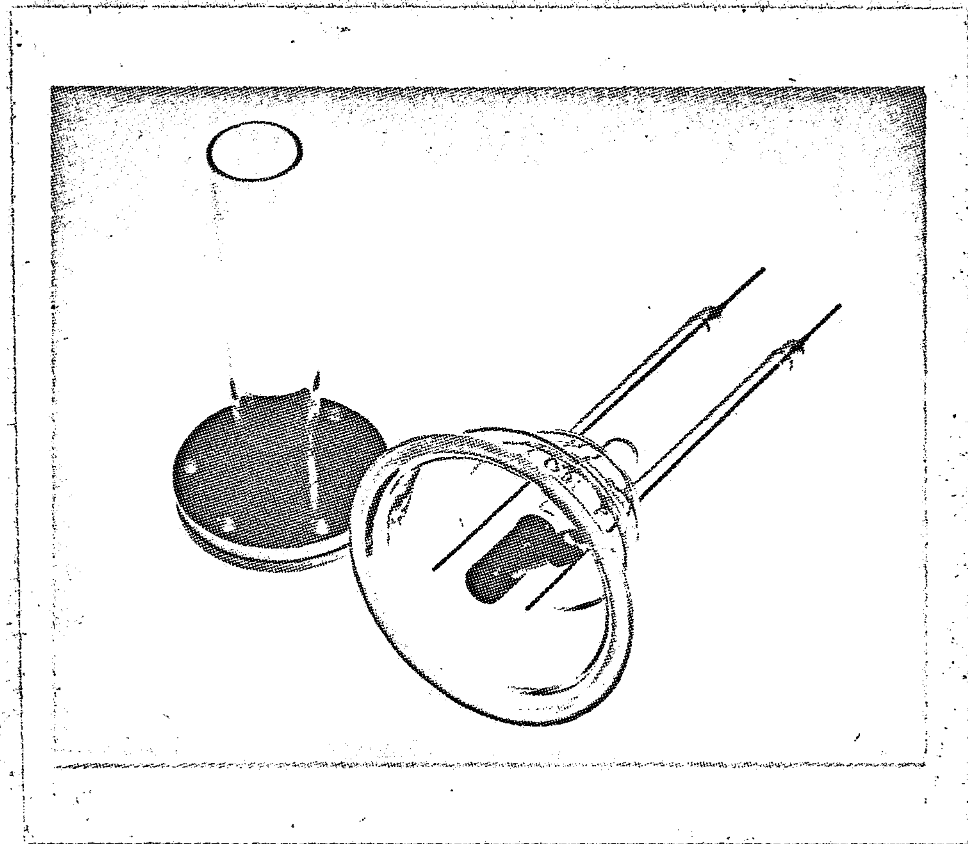
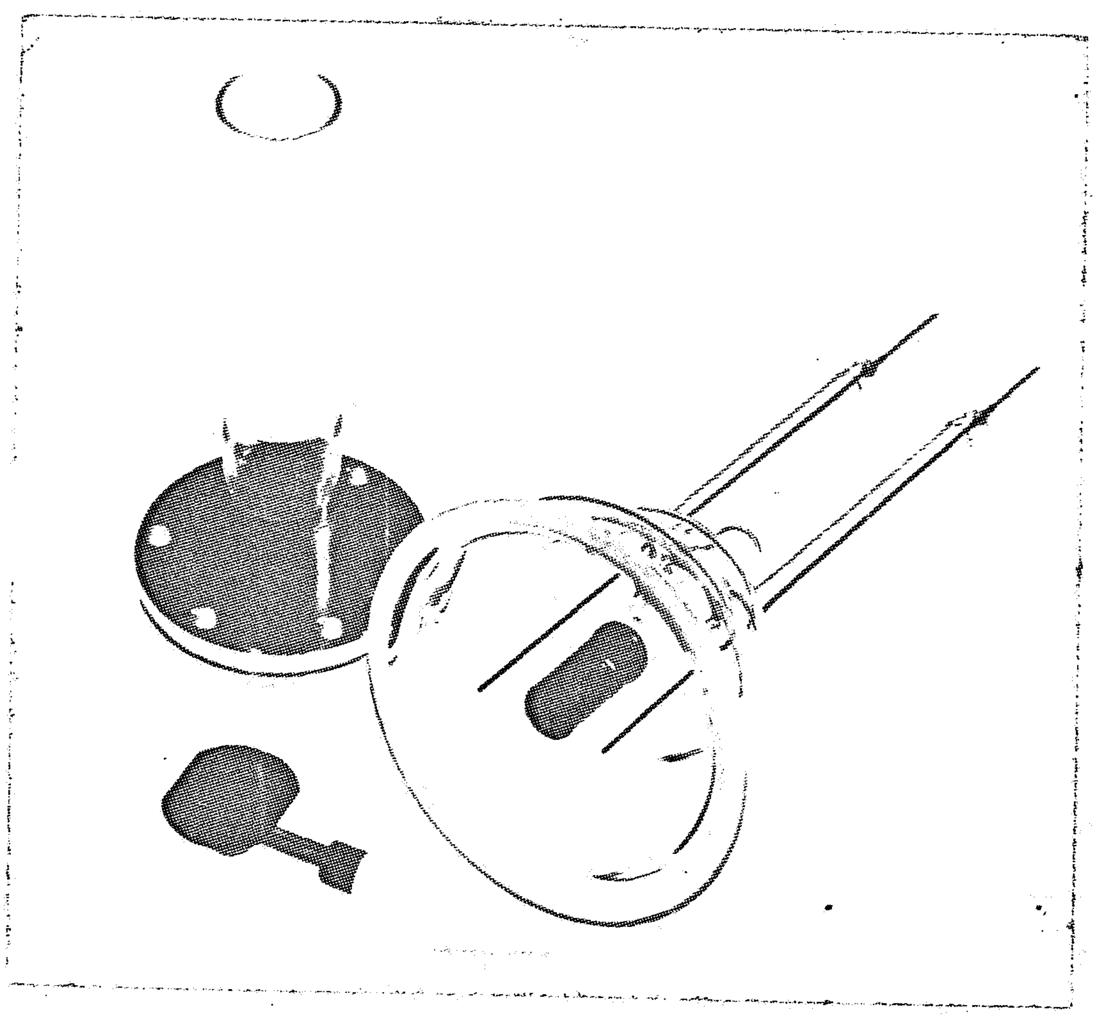
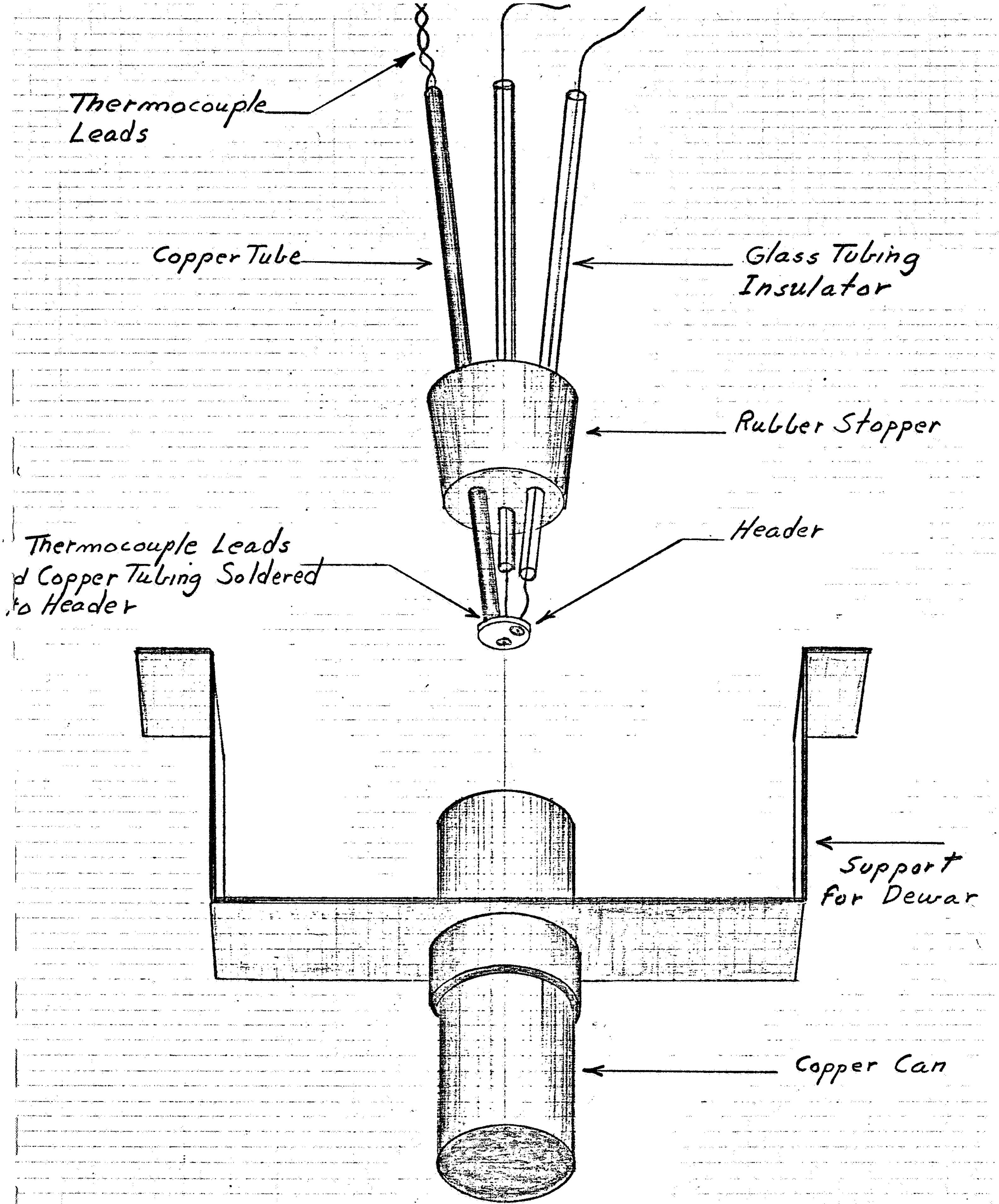


Fig 1





Thermocouple Leads
Copper Tube
Glass Tubing Insulator
Rubber Stopper
Header
Thermocouple Leads
d Copper Tubing Soldered
to Header
Support for Dewar
Copper Can

Fig. 2

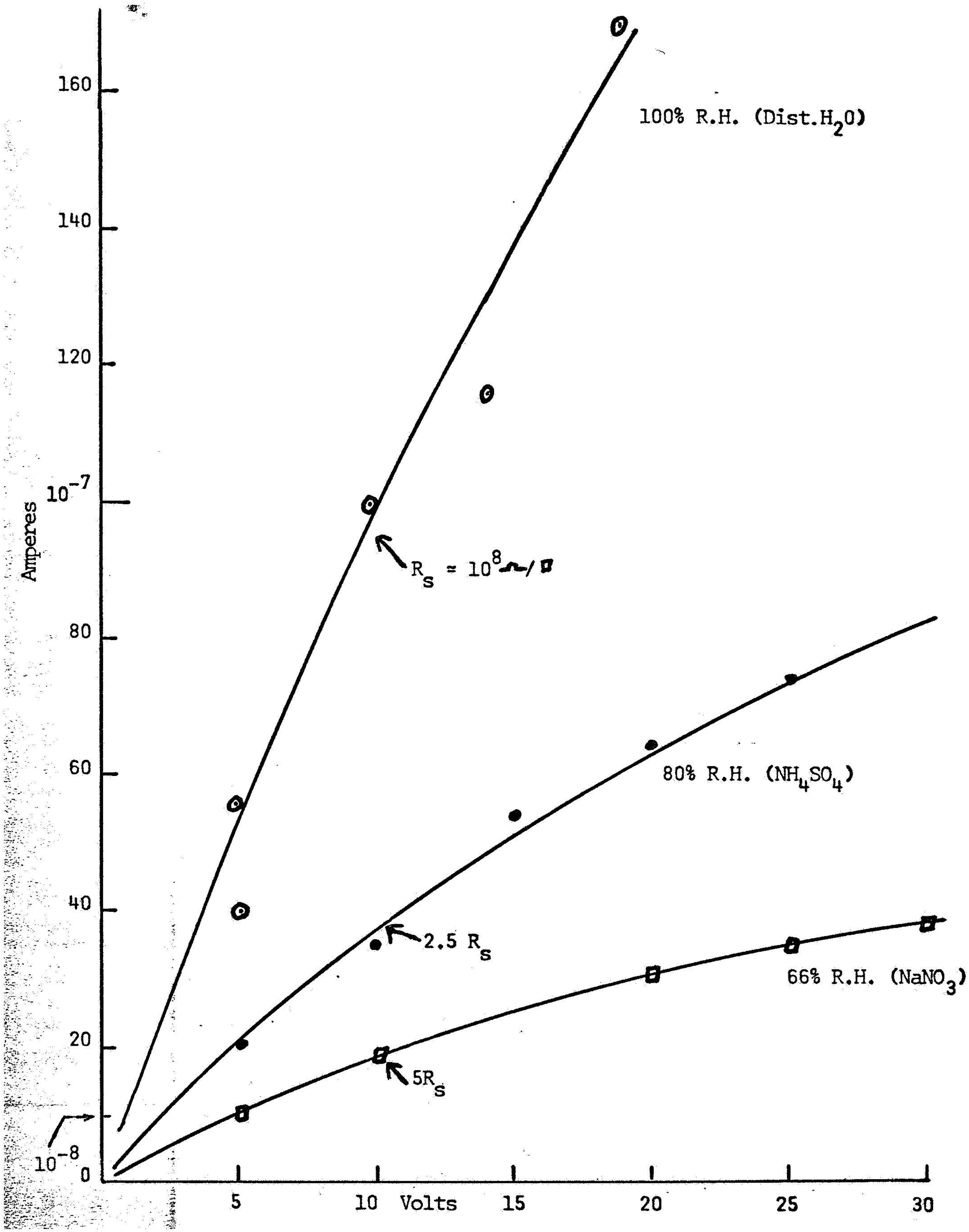

160
140
120
10^-7
80
60
40
20
10^-8
0
Amperes
5
10 Volts
15
20
25
30
100% R.H. (Dist.H2O)
80% R.H. (NH4SO4)
66% R.H. (NaNO3)
Rs = 10^8 Ω/□
2.5 Rs
5Rs

Fig. 3

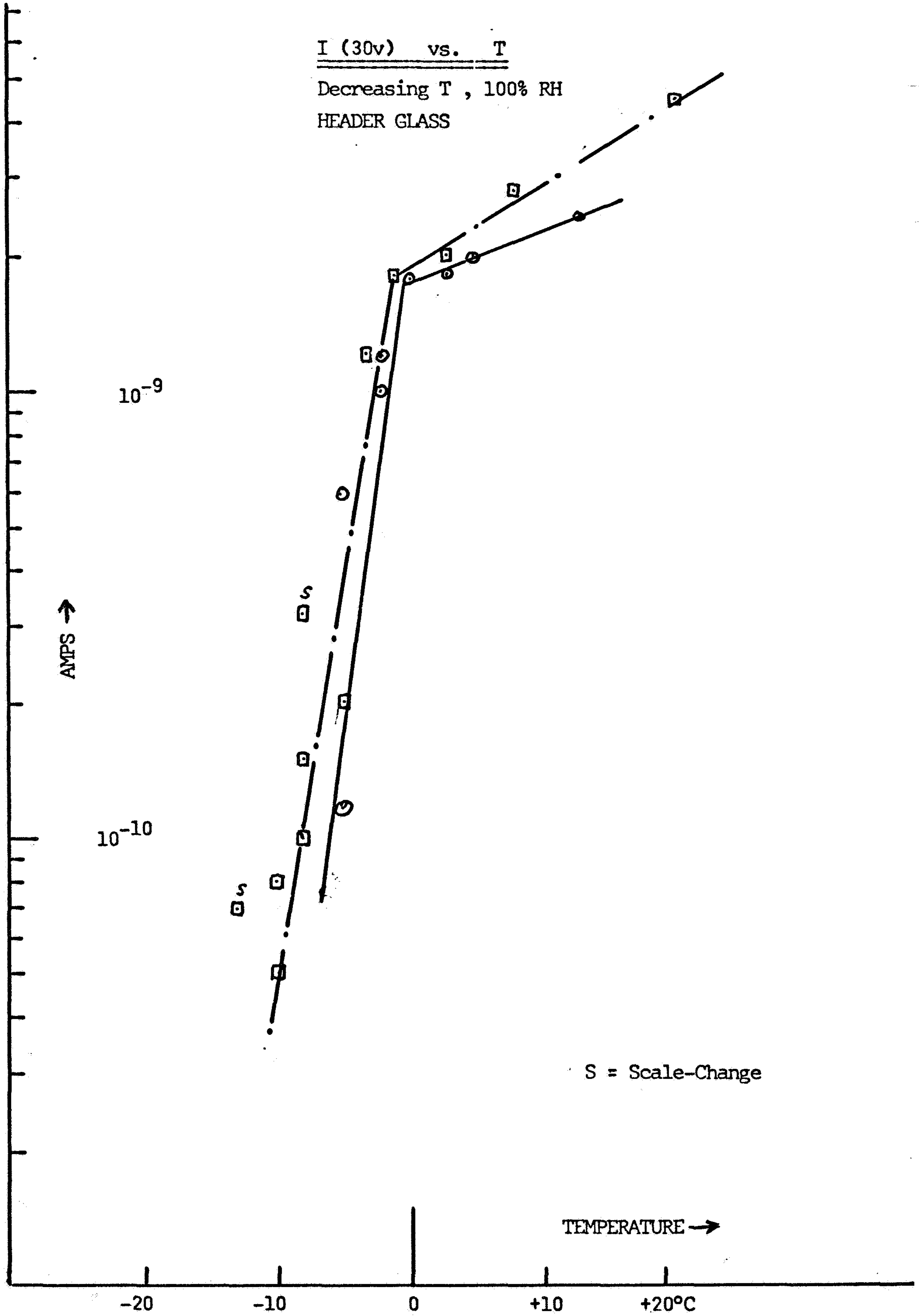

I (30v) vs. T
Decreasing T , 100% RH
HEADER GLASS
10^{-9}
10^{-10}
AMPS
S
S
S = Scale-Change
TEMPERATURE
-20
-10
0
+10
+20°C

Fig. 4

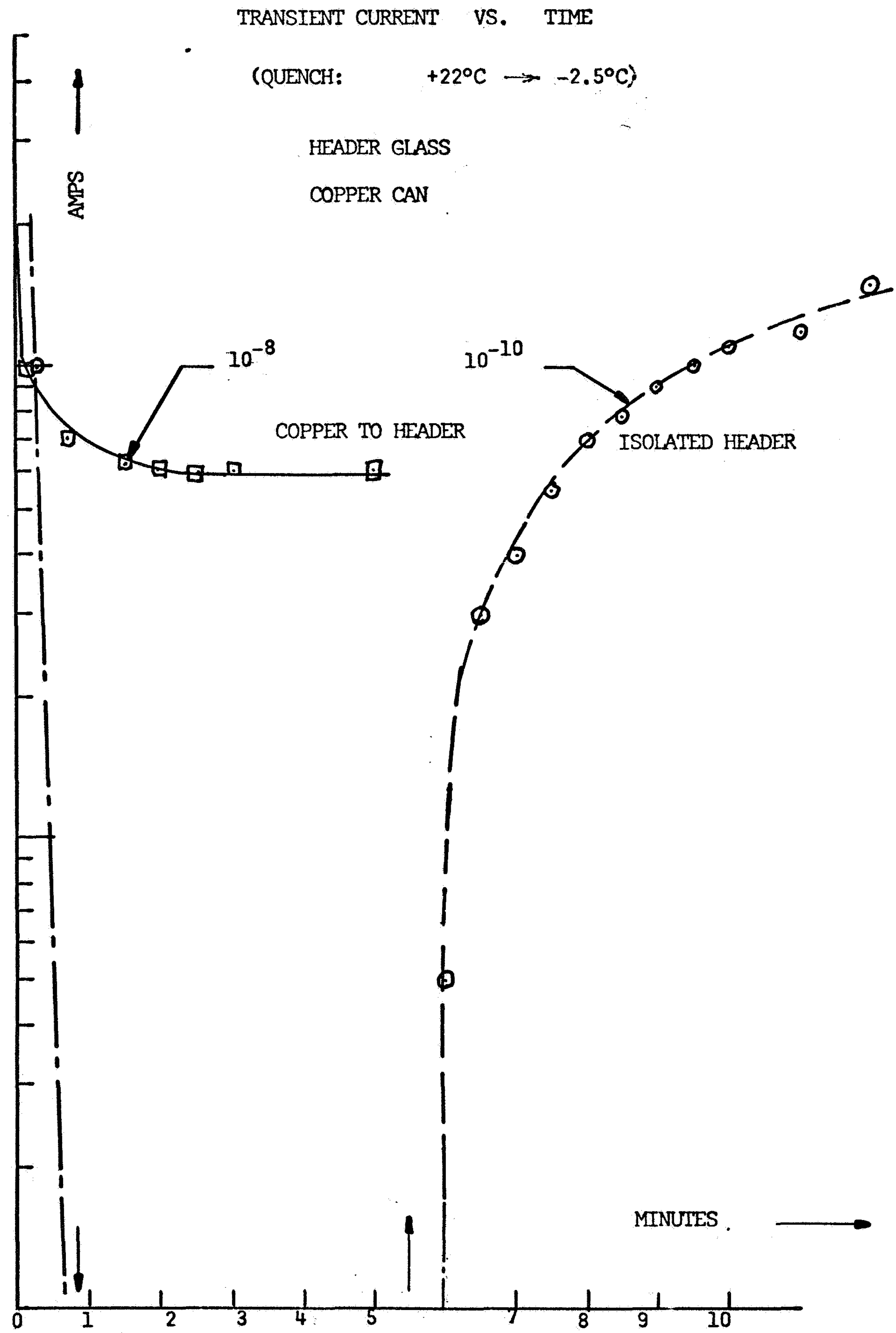
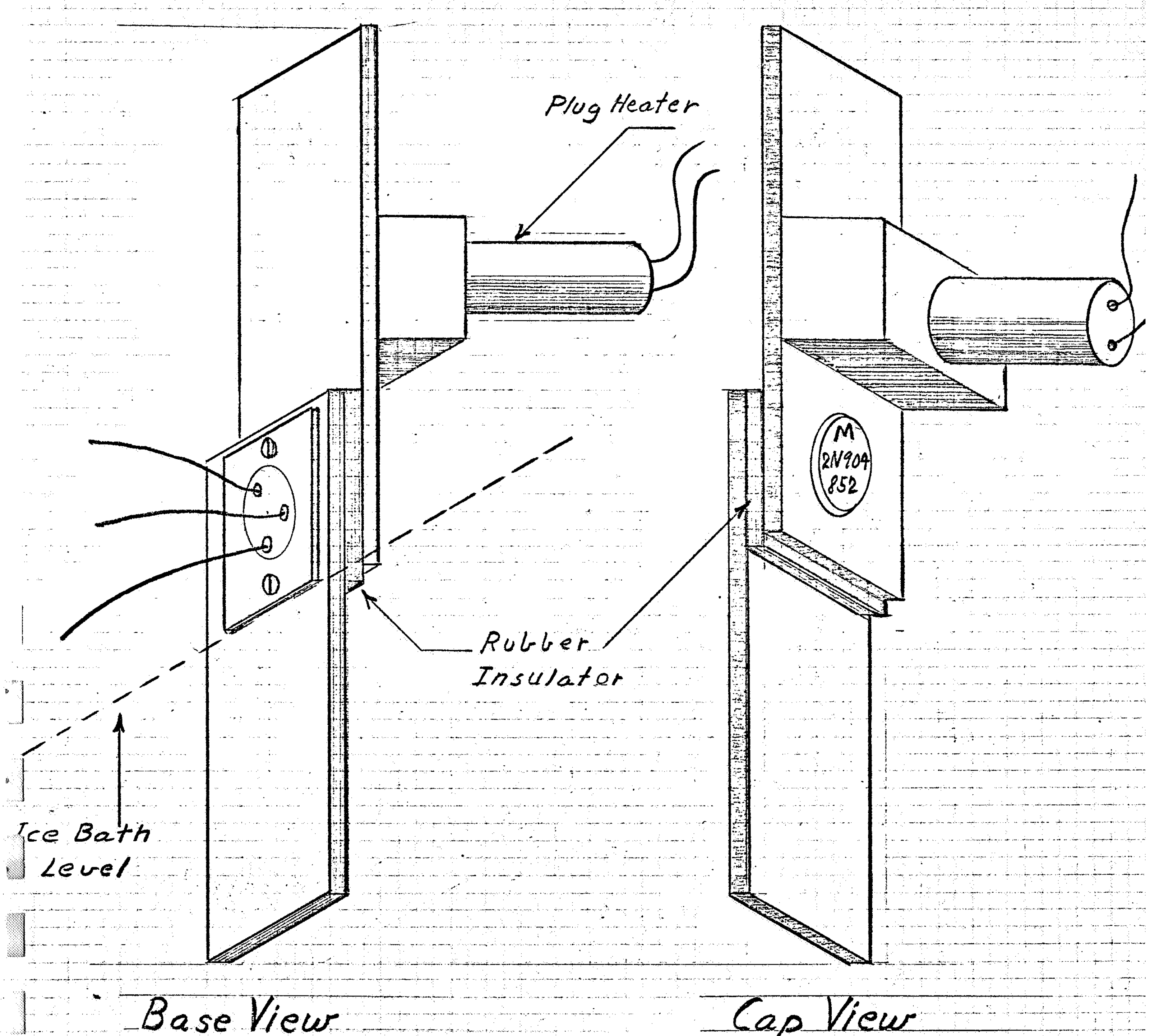
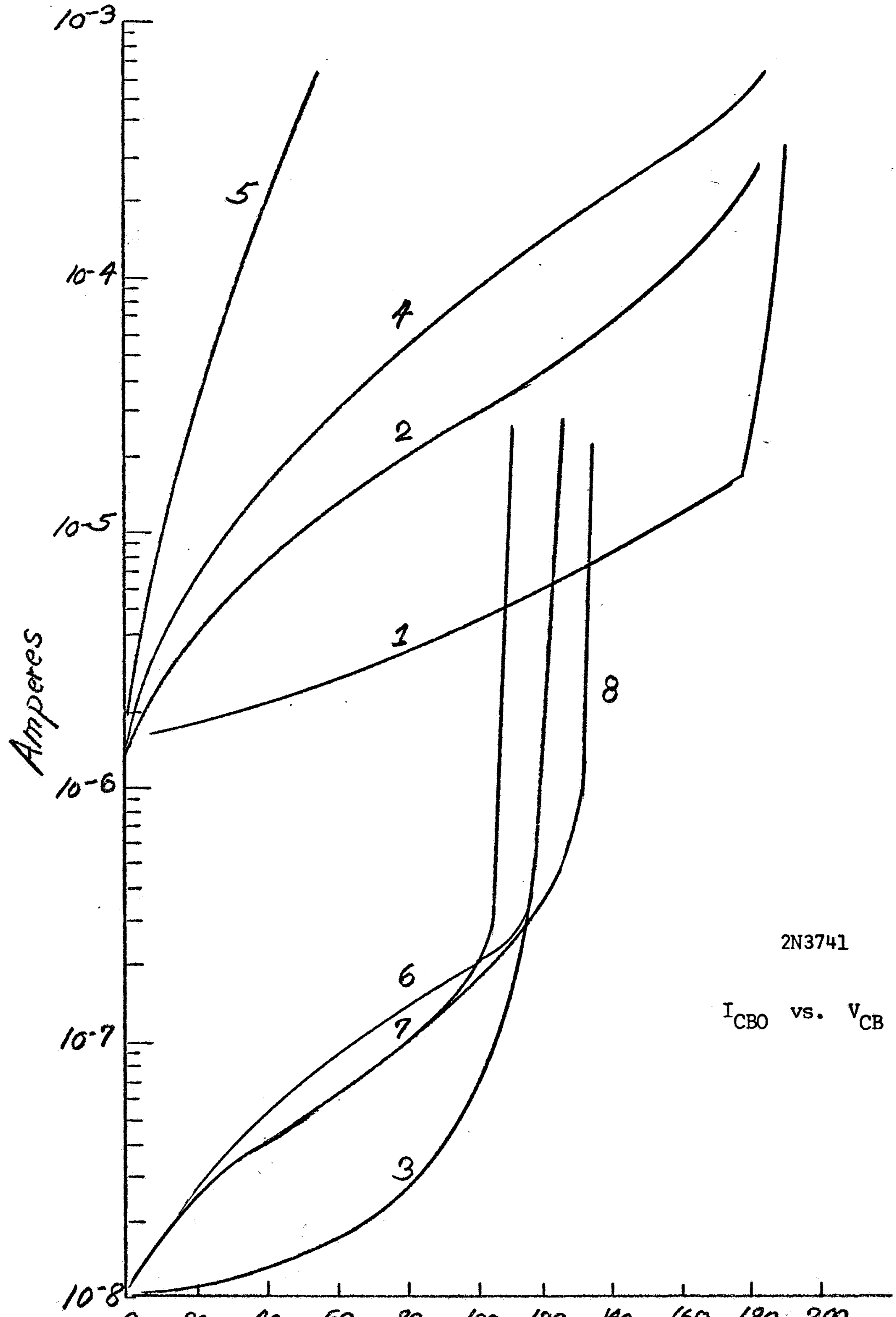

TRANSIENT CURRENT VS. TIME
(QUENCH: +22°C → -2.5°C)
HEADER GLASS
COPPER CAN
AMPS
10^-8
COPPER TO HEADER
10^-10
ISOLATED HEADER
MINUTES
0
1
2
3
4
5
7
8
9
10

Fig. 5



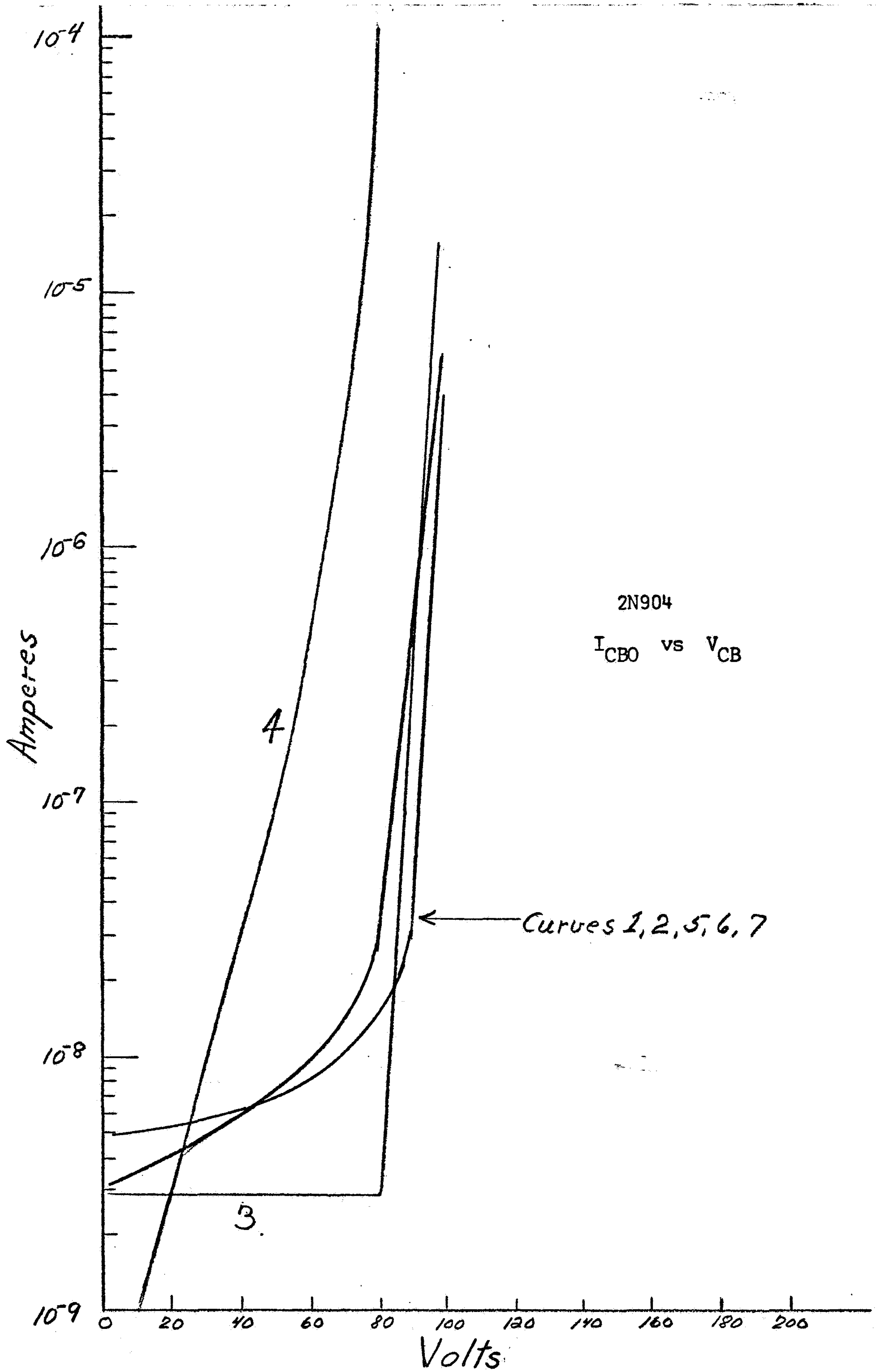
Plug Heater
M
2N904
852
Rubber
Insulator
Ice Bath
Level
Base View
Cap View

Fig. 6



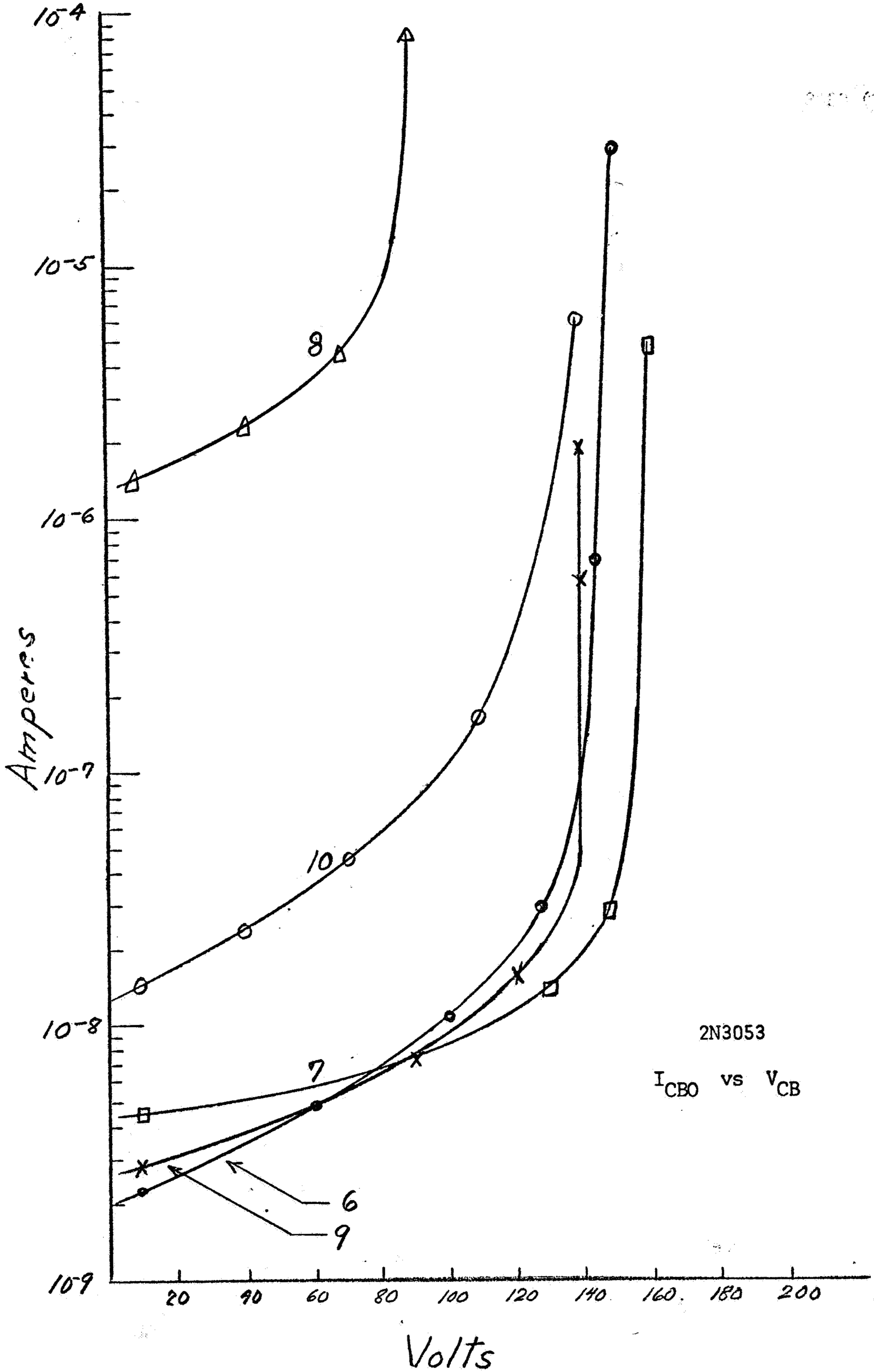
10-3
10-4
10-5
10-6
10-7
10-8
Amperes
0
20
40
60
80
100
120
140
160
180
200
Volts
5
4
2
1
8
6
7
3
2N3741
I_CBO vs. V_CB

Fig. 7



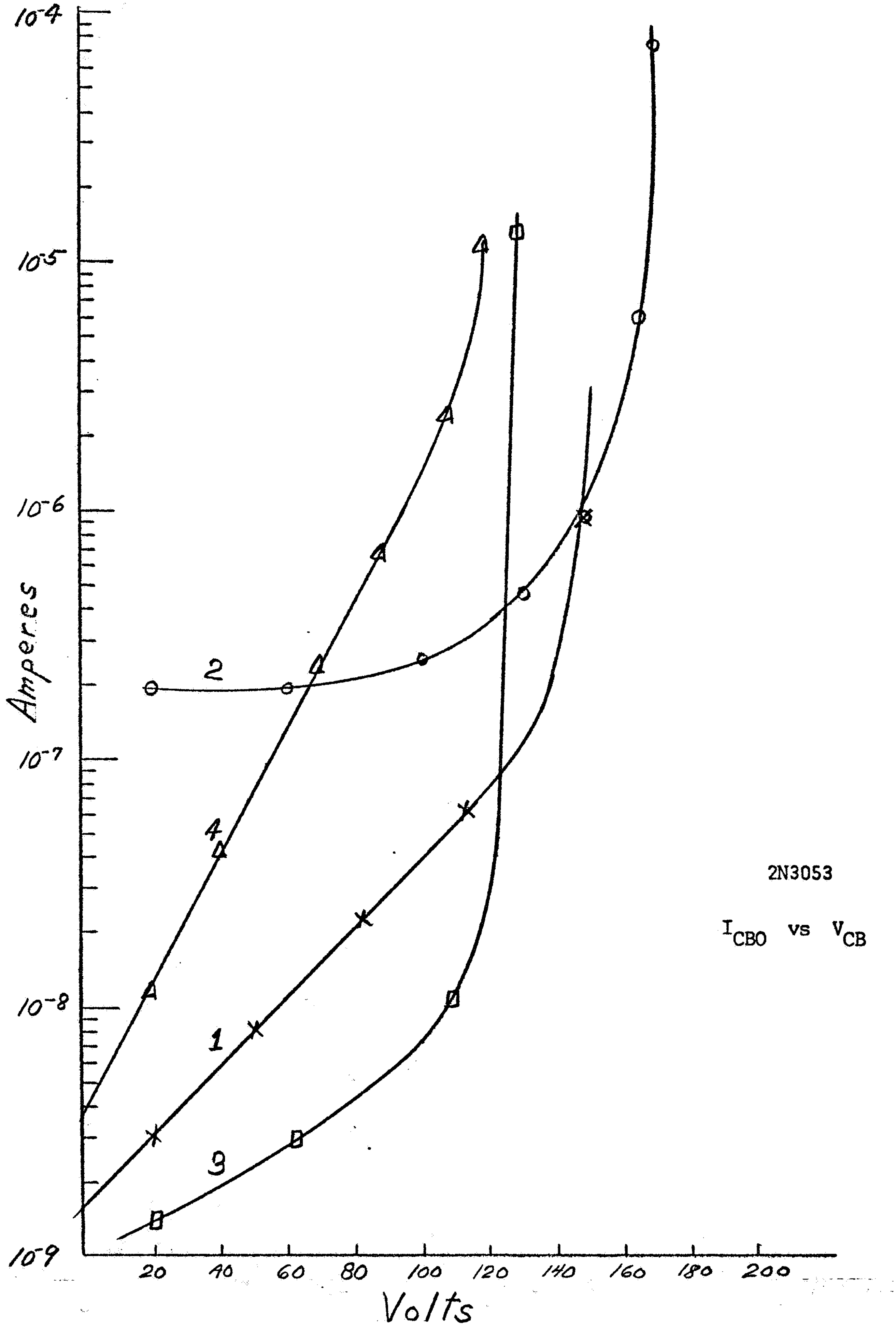
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
Amperes
4
3.
Curves 1, 2, 5, 6, 7
2N904
I_{CBO} vs V_{CB}
0
20
40
60
80
100
120
140
160
180
200
Volts

Fig. 8



10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
Amperes
8
10
7
6
9
2N3053
I_{CBO} vs V_{CB}
20
40
60
80
100
120
140
160
180
200
Volts

Fig. 9



10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
Amperes
2
4
1
3
20
40
60
80
100
120
140
160
180
200
Volts
2N3053
I_{CBO} vs V_{CB}

Fig. 10

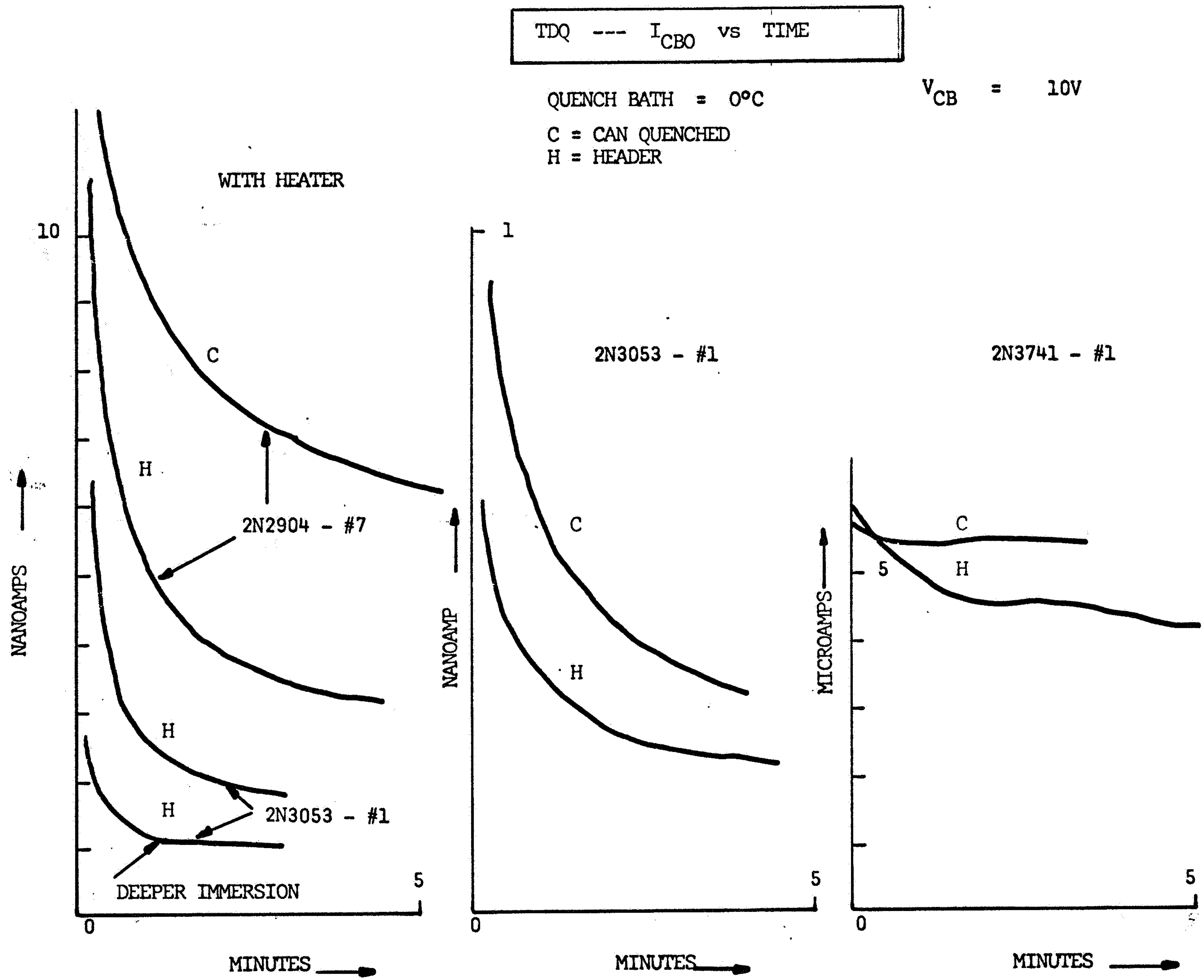

TDQ --- I_{CBO} vs TIME
QUENCH BATH = 0°C
C = CAN QUENCHED
H = HEADER
V_{CB} = 10V
WITH HEATER
10
NANOAMPS
C
H
2N2904 - #7
H
H
2N3053 - #1
DEEPER IMMERSION
0
5
MINUTES
1
NANOAMP
2N3053 - #1
C
H
0
5
MINUTES
2N3741 - #1
MICROAMPS
C
5
H
0
5
MINUTES

Fig. 11

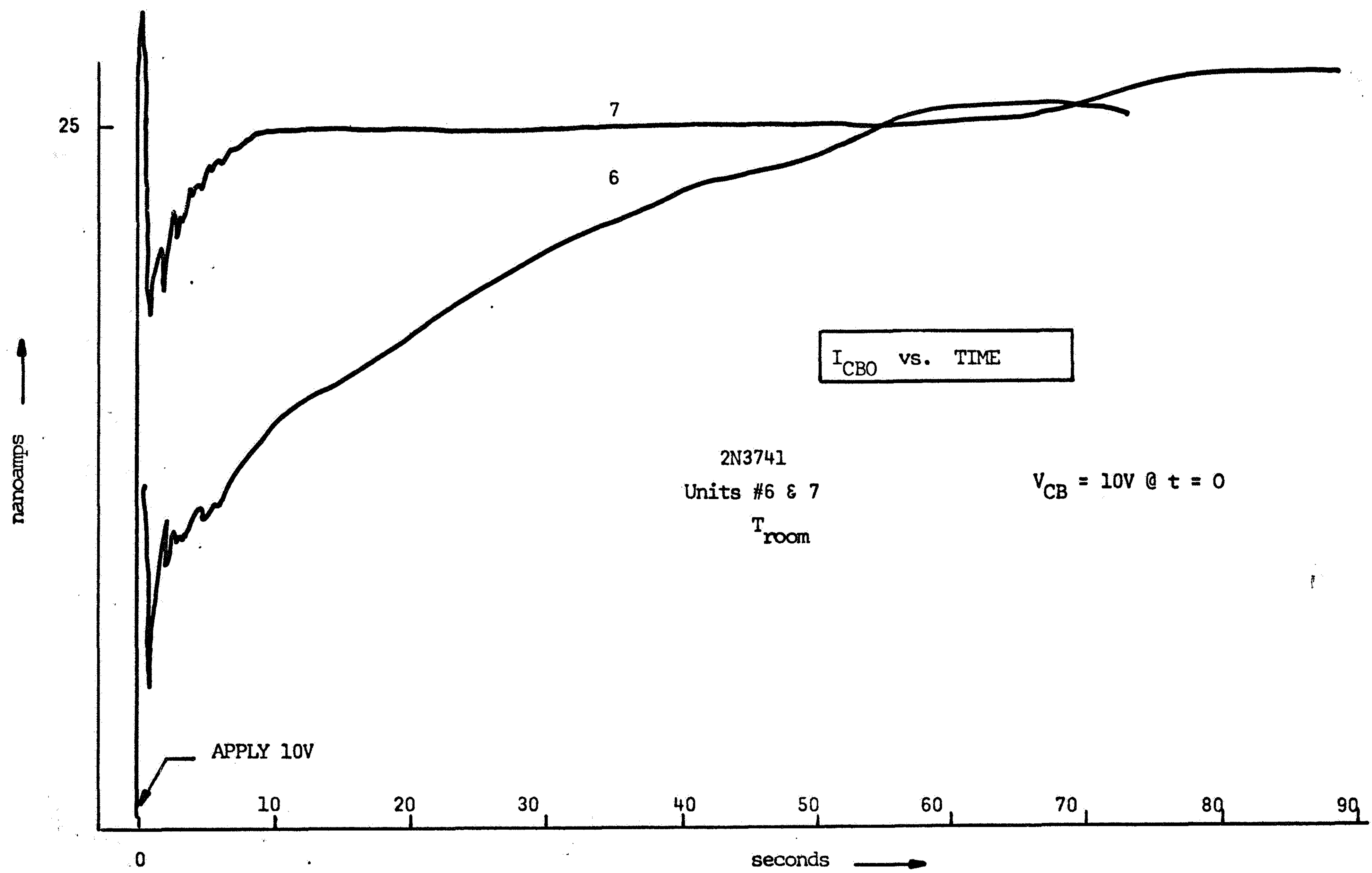
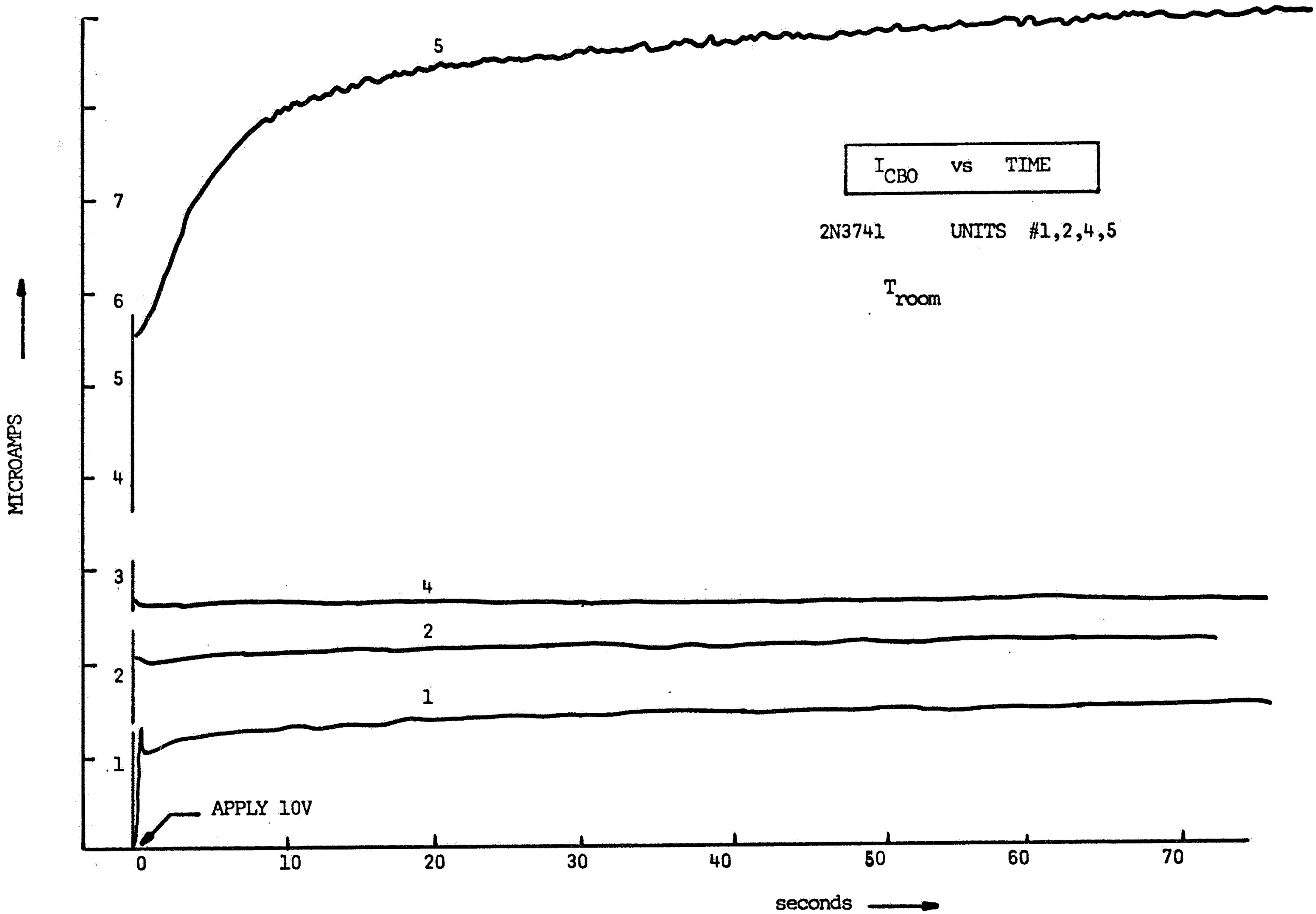

7
6
25
nanoamps
I_{CBO} vs. TIME
2N3741
Units #6 & 7
T_{room}
V_{CB} = 10V @ t = 0
APPLY 10V
0
10
20
30
40
50
60
70
80
90
seconds

Fig. 12



ICBO vs TIME
2N3741 UNITS #1,2,4,5
Troom
MICROAMPS
seconds
APPLY 10V
5
4
2
1
0
10
20
30
40
50
60
70

Fig. 13

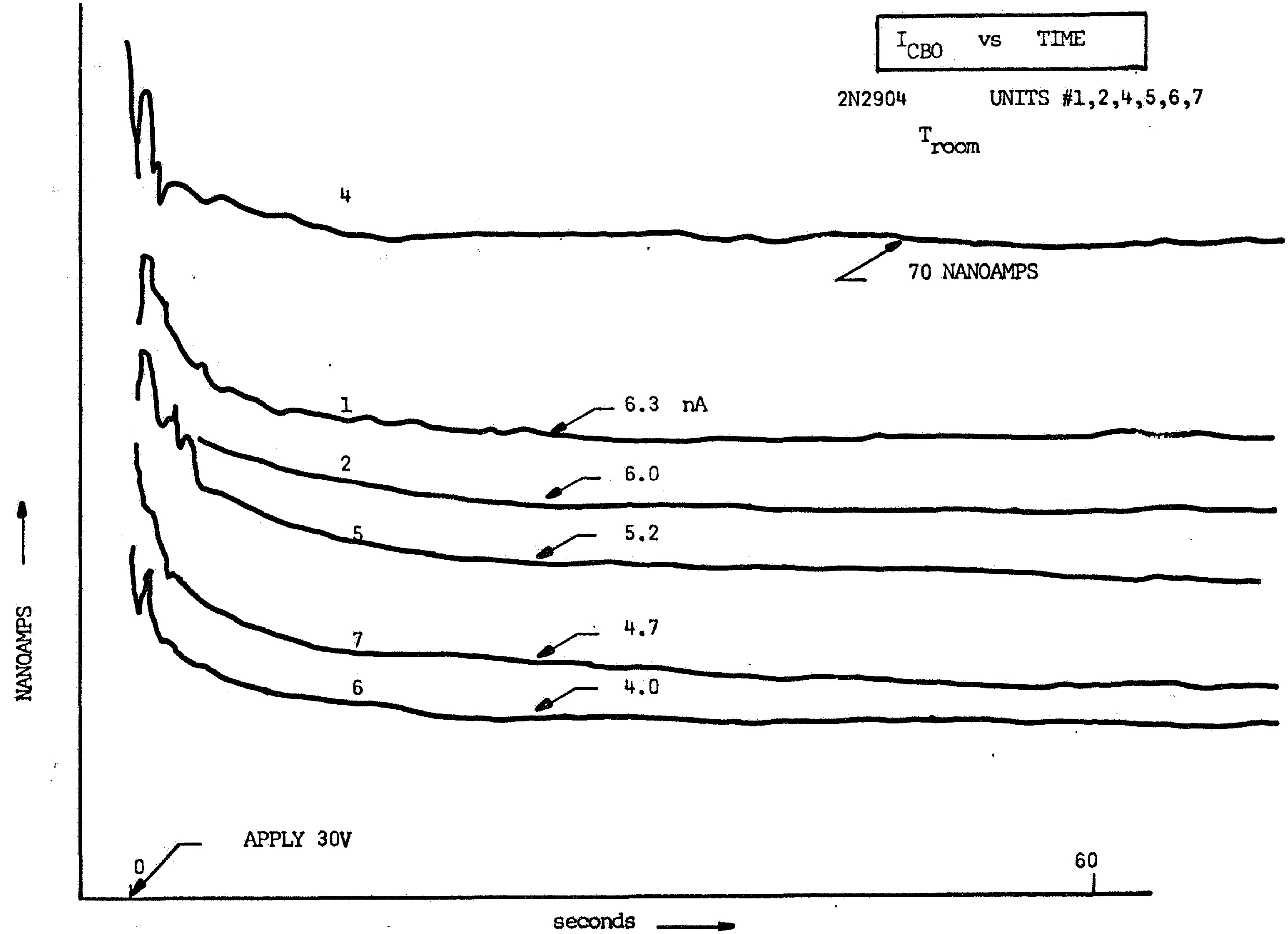
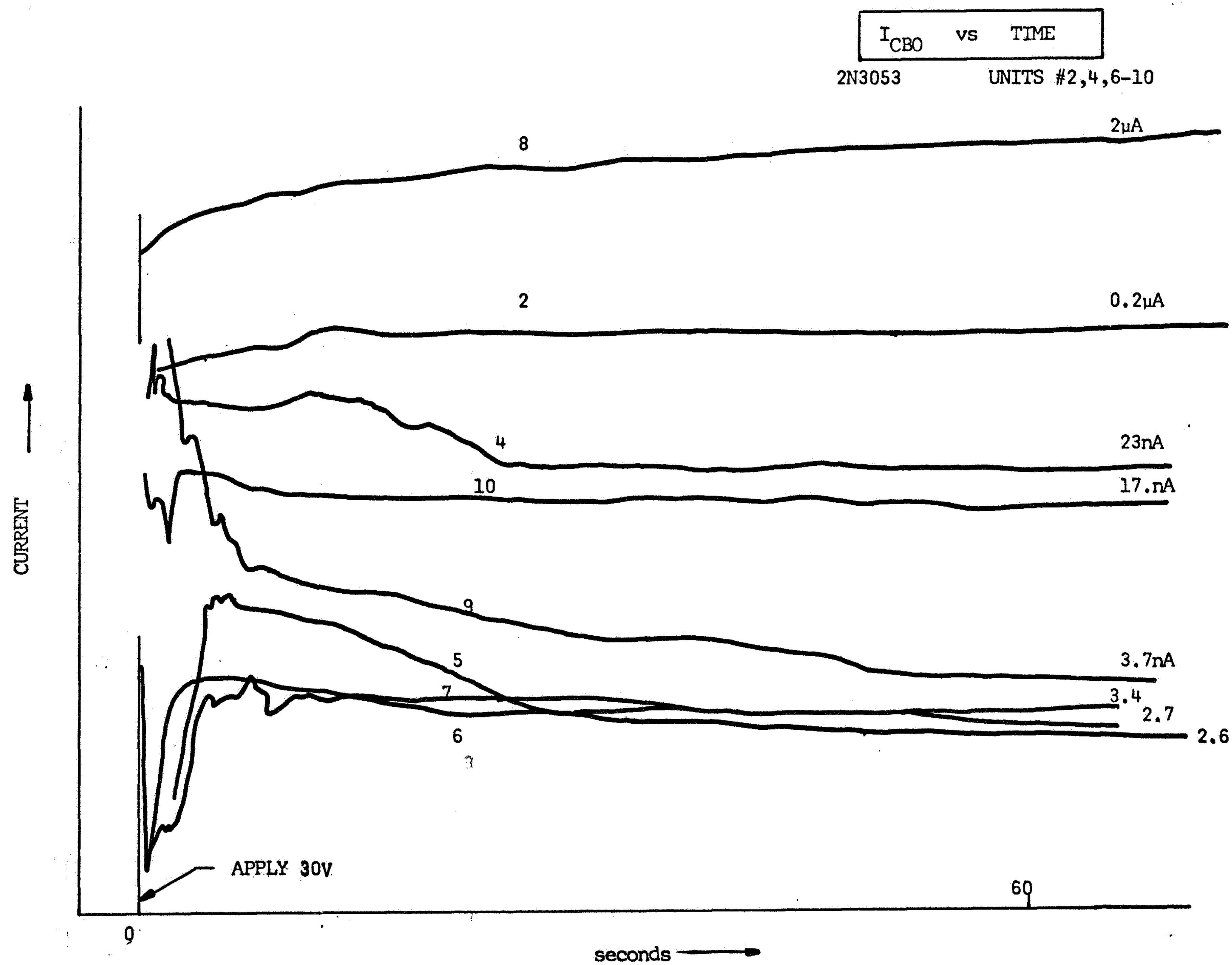

I_{CBO} vs TIME
2N2904 UNITS #1,2,4,5,6,7
T_{room}
4
70 NANOAMPS
1
6.3 nA
2
6.0
5
5.2
7
4.7
6
4.0
NANOAMPS
APPLY 30V
0
60
seconds

Fig. 14



I_{CBO} vs TIME
2N3053
UNITS #2,4,6-10
CURRENT
8
2μA
2
0.2μA
4
23nA
10
17.nA
9
3.7nA
5
7
6
3.4
2.7
2.6
APPLY 30V
0
60
seconds

Fig. 15

EFFECT OF TEMPERATURE

I_{CBO} vs TIME

2N3741 UNIT #1 at 0°C and T_{room}

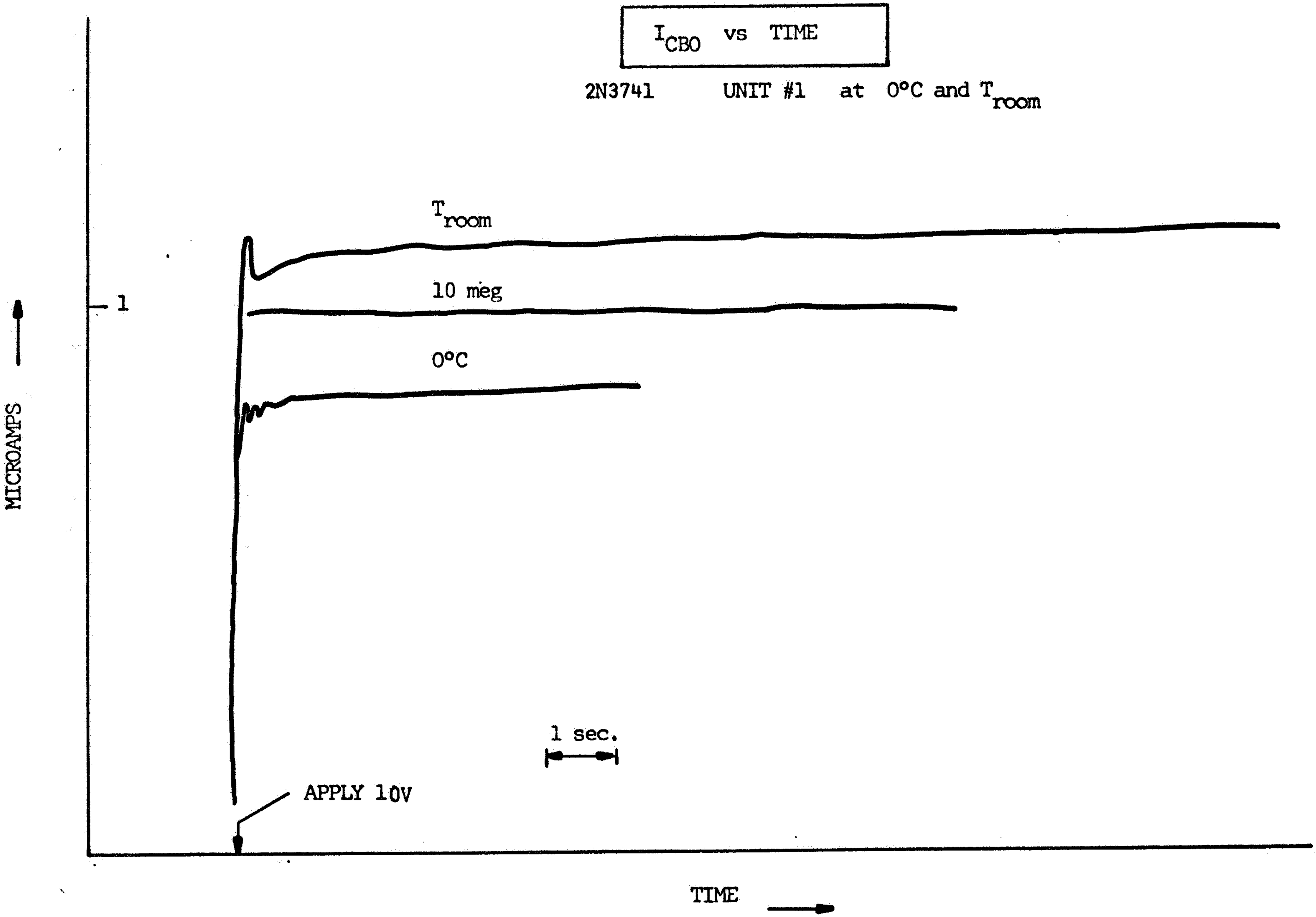


Fig. 16

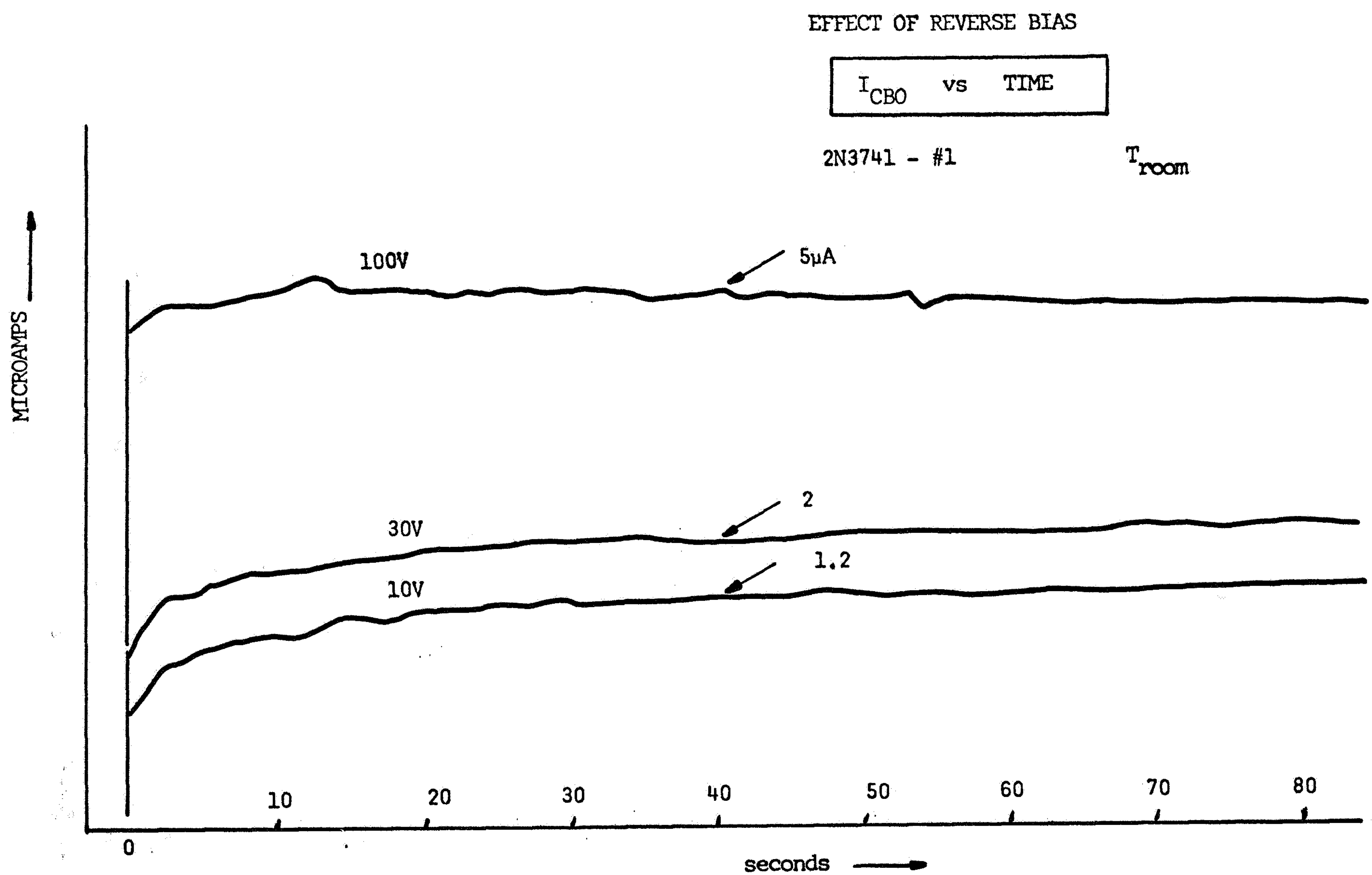
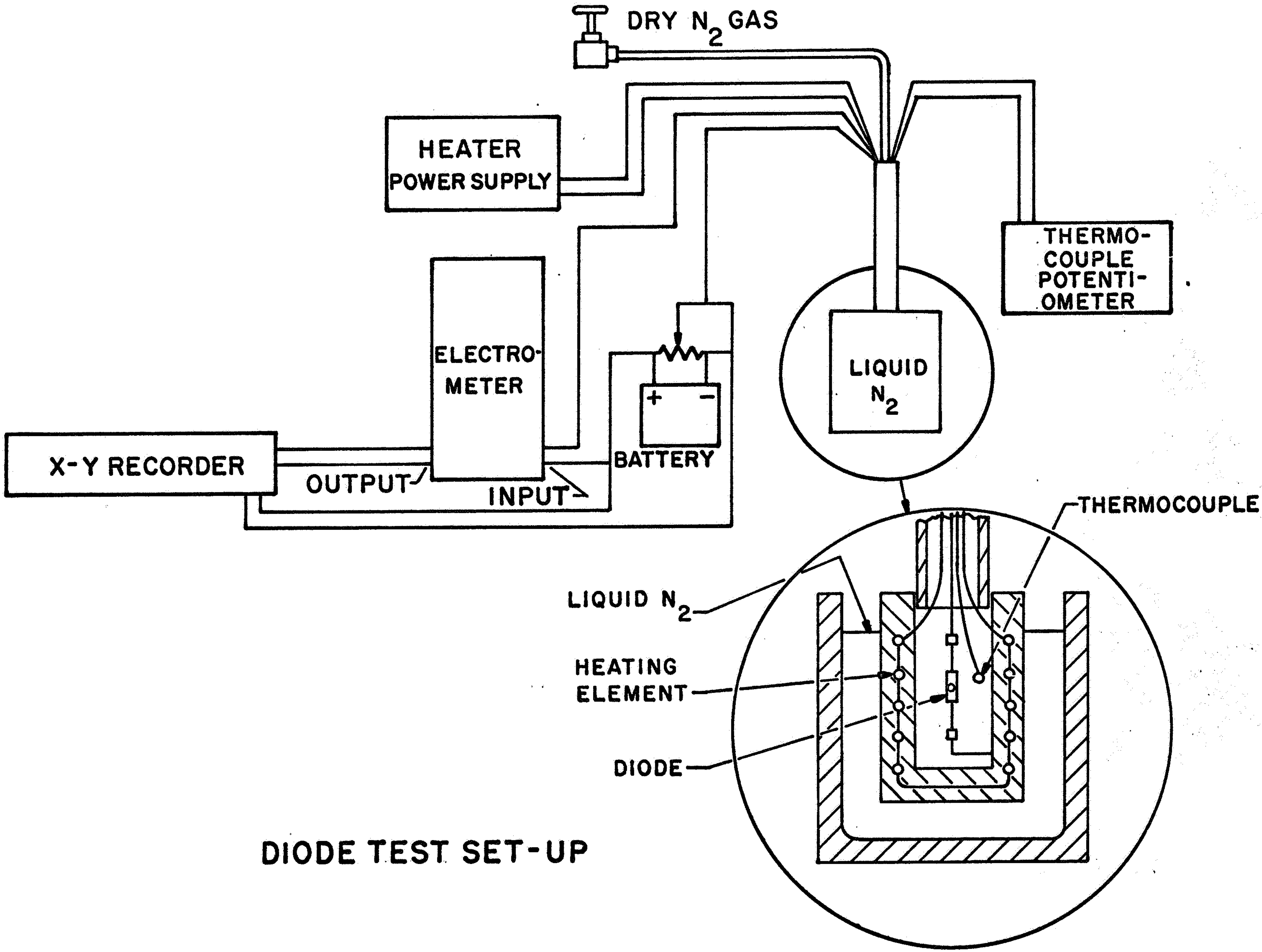

EFFECT OF REVERSE BIAS
I_{CBO} vs TIME
2N3741 - #1
T_{room}
MICROAMPS
100V
5μA
30V
2
10V
1.2
0
10
20
30
40
50
60
70
80
seconds

Fig. 17



DIODE TEST SET-UP

Fig. 18

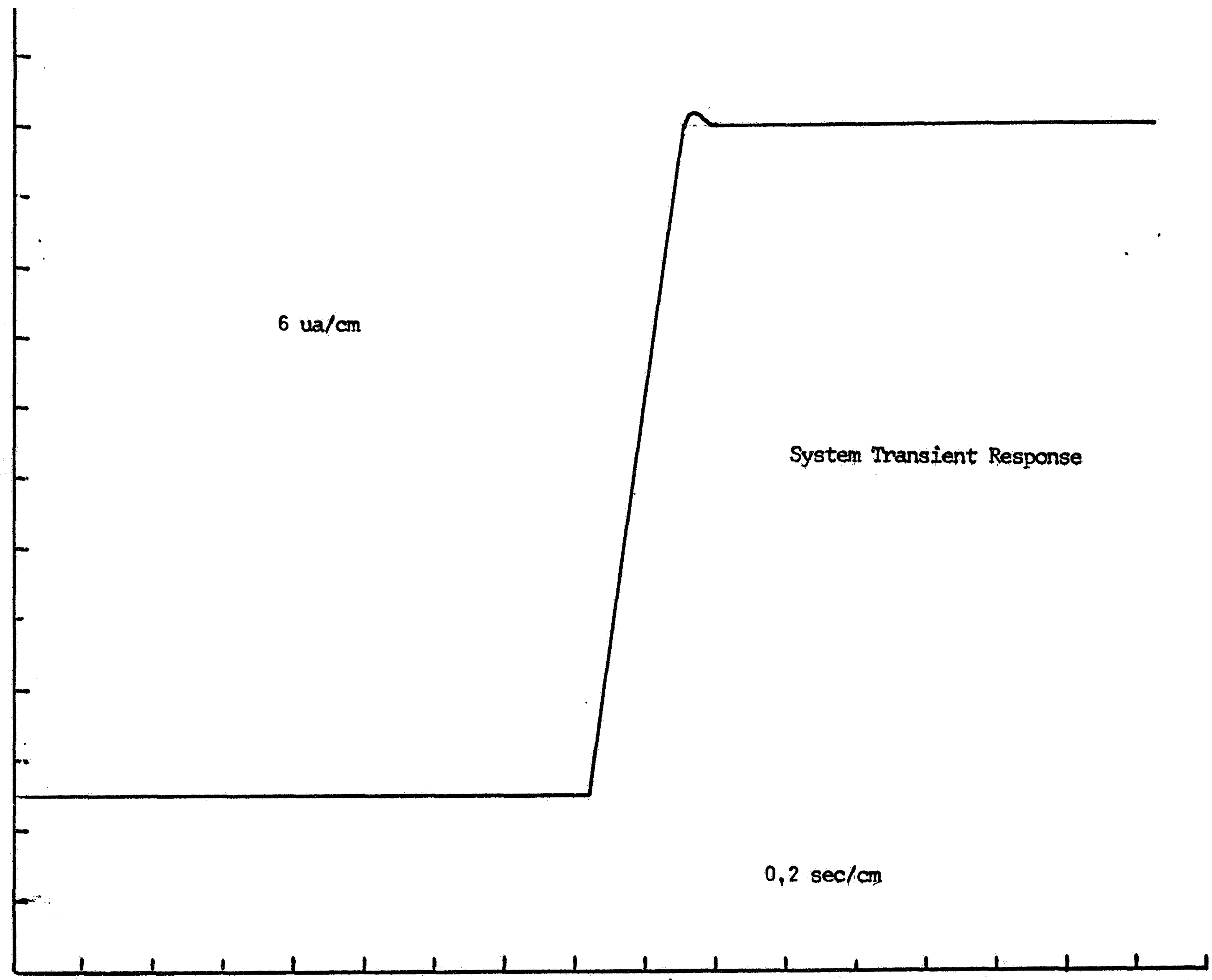


Fig. 19

Reversal Of Hysteresis As A Function Of Temperature

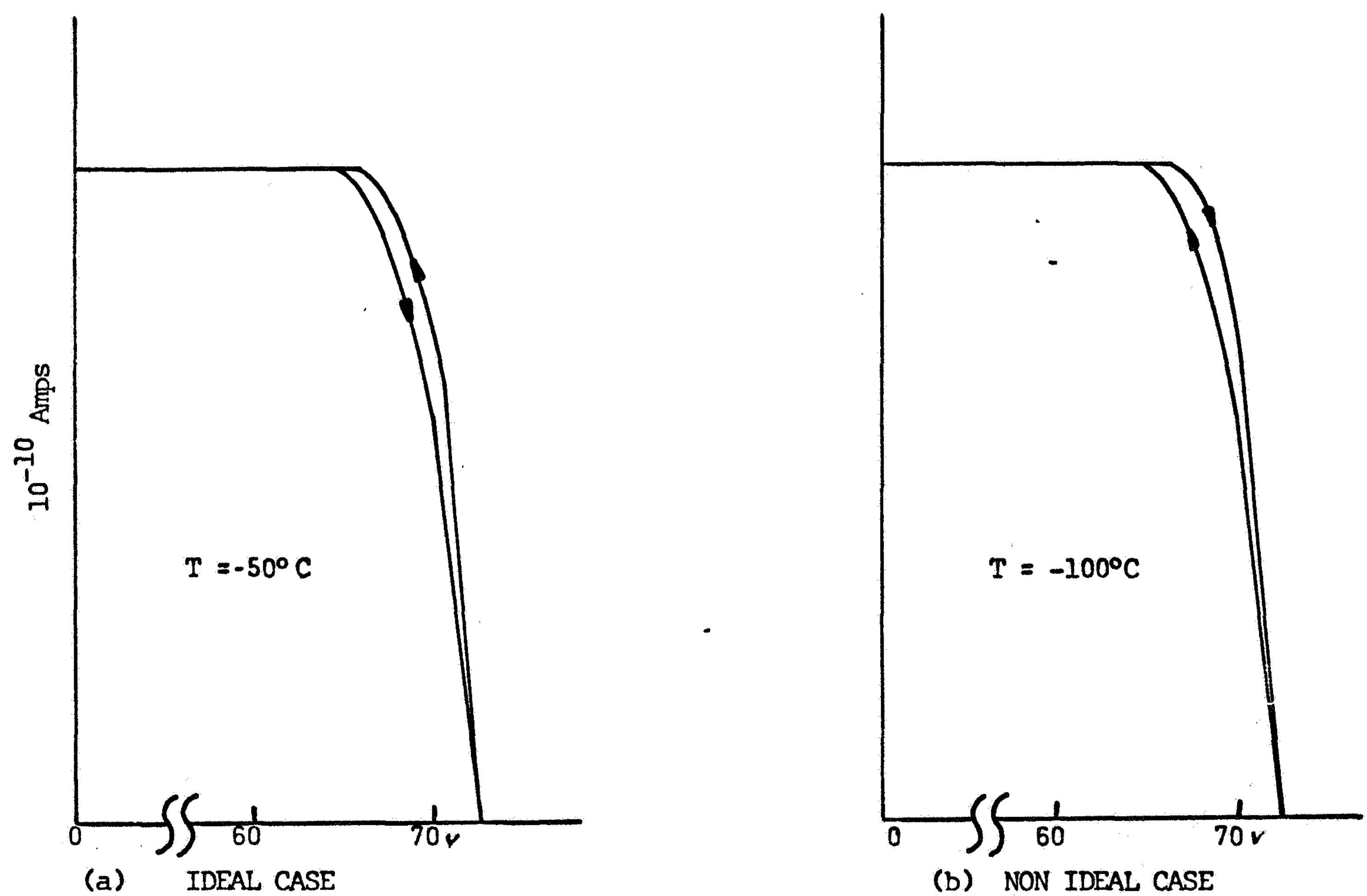


Fig. 20